Evaluation of groundwater chemistry affected by an abandoned metal mine within a dam construction site, South Korea

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Abstract

Groundwater chemistry in and around an abandoned metal mine within a large dam construction site was evaluated. For this purpose, a total of 50 groundwater samples were collected and chemically analysed for major ions and toxic metals. The pHs of the groundwaters were near neutral to slightly basic, with an apparent increase along the flow direction away from the mine waste dump. Higher values of electrical conductivity with a mean of 532 μS cm^{-1} were observed in the mine area. Dissolved oxygen concentrations over 5 mg l^{-1} clearly indicated an oxygenated groundwater environment. The high concentration of sulphate was derived from weathering and oxidation of sulphide minerals. Hydrochemistry of the groundwater samples is characterized by the relatively significant enrichment of Ca^{2+} and SO_4^{2-}. Results of factor analysis also indicated that the dominant mechanisms or continuing processes affecting the distribution of the chemical parameters in the study area are various geochemical reactions including dissolution of sulphide and carbonate minerals, and removal of calcium and sulphate by dilution through mixing with Ca^{2+}– and SO_4^{2-}-poor groundwaters. In the mine area, substantial groundwater contamination by toxic metals including Zn, Al, Fe and Mn was observed. Most of the toxic metals decreased gradually or dramatically with distance from the mine, although some metals were also found in high concentrations in the downstream areas. Compared with the contamination levels of the surrounding farmland soils and stream sediments, the levels of contamination of groundwater by toxic metals were relatively low. The low concentrations are ascribed to the high pH and highly oxygenated conditions, which reduce toxic metal mobility. Significant groundwater contamination with toxic metals was strictly limited within the immediate vicinity of the mine waste dump but the ubiquitous distribution of the toxic metals with slightly elevated levels all over the study area may be attributed to the same geology and mineralogy as in the mine area.

Keywords: factor and cluster analyses, abandoned mine, sulphate, zinc, toxic metals, Korea

Instances of soil and groundwater contamination by toxic metals at abandoned metal mines are markedly increasing in South Korea (Lee *et al.* 2004). Acid mine drainage from the iron sulphide minerals pyrite and less commonly marcasite typically contains elevated concentrations of SO_4, Fe, Mn, Al and other toxic metals (Taylor & Shuman 1988; Pietz *et al.* 1989; Pérez & Calvo 1992; Rose & Cravotta 1998; Clark *et al.* 2001; Younger *et al.* 2002). This drew the attention of the environmental community to the study of site investigation and remediation technologies. In particular, abandoned mines located within or upgradient of a dam construction site have caused public disquiet. There are a large number of metal mines (over 1500), scattered all over the country, most of which were abandoned mainly because exhaustion of ore minerals. These abandoned and non-remediated mines including tailings and spoil piles, which impose a heavy burden on the local government and relevant environmental authorities.

As a water-poor country, South Korea is planning to construct additionally at least 12 medium-sized dams for water storage throughout the country. One of the difficult problems the construction and environmental authorities nearly always encounter is the presence of abandoned metal mines within the planned dam construction areas. Therefore appropriate environmental investigation and remediation measures are essentially required. For instance, 42.4 million dollars will be spent for the remediation of contaminated soil and groundwaters for the study site, which is a significant portion of the total dam construction budget. In another dam construction site, much more money (about 100 million dollars) was spent to resolve the same problem. Hence, the economic burden caused by abandoned mines is prompting relevant environmental studies for dam construction sites. This study was one of these efforts.

In addition, as noted above, there are a large number of abandoned metal mines and a large proportion of the mines need urgent or stepwise remediation action. Central and local governments are therefore making plans and budgets for the remediation. It is reported by the Ministry of Environment of South Korea that an average of 8.5 million dollars is needed for the remediation per single mine site (excepting dam construction

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sites). For the present, the local and central governments share the expenses evenly with each other.

Many studies concerning contamination problems derived from mining activities have been undertaken, focusing variously on soils, plants, surface or stream waters, or stream sediments (Bayless & Olyphant 1993; Benvenuti *et al.* 1995; Wood *et al.* 1999; Bowell 2001; Marques *et al.* 2001; Banwart *et al.* 2002; Bell *et al.* 2002; Younger *et al.* 2002; Gandy & Younger 2003; Miller *et al.* 2004). However, despite the large values of the remediation budgets, studies or information on toxic metal concentrations, chemical compositions of groundwaters, hydrogeological conditions, and available remediation technologies for abandoned metalliferous mines are as yet scarce in South Korea. The objectives of this study are thus to examine the chemical compositions of the groundwaters and the extent and degree of toxic metal contamination, to evaluate the differences in chemical compositions of the groundwaters sampled from the mining influenced area and a control or background area using multivariate statistical analysis, and to provide the basic information needed to identify a suitable remediation approach for the contamination.

Regional hydrogeology

The study area including an abandoned zinc mine is located in the southeastern part of South Korea (Fig. 1). The mine was operated from 1964 to 1972. The mineralization, classified as a hydrothermal replacement type, contains sphalerite, galena and chalcopyrite, with a small amount of pyrite and arsenopyrite. The mine is in an area of mountainous geomorphology, with rounded rolling hills and narrow valleys that form a dendritic type drainage network. The closure of the mining activity left about 23 000 tons of waste rocks and tailings. During the period of 1998–1999, to tackle potential environmental problems from the mining wastes, the provincial authority conducted an environmental treatment measure including installation of drain ditch, surface plant cover, containment–barrier wall and subsequent reclamation mainly focused on the mining waste site (see Fig. 1). However, the mining wastes had been dispersed downslope by surface runoff mainly as a result of heavy rainfall, wind action and draining effluent, and had contaminated paddy fields, stream sediments and stream waters.

The study site is underlain by the Gyeongsang sedimentary formation and the geology in and around the mine is greatly influenced by Cretaceous igneous activity. The sedimentary formation is mainly composed of sandstone, shale and conglomerate, which were metamorphosed by the igneous rocks. The igneous rocks are Cretaceous quartz porphyry, rhyolite, intermediate dykes and granites. In the streams and lowlands, alluvial and colluvial deposits unconformably overlie the bedrocks. The main streams and creeks run from NE to SW (see Fig. 1). A large number of branch streams converge with the main stream. Although the study area is sparsely populated, with settlements mainly along the streams, there are several private and public groundwater wells for domestic use, because of the lack of networked supplies in the area. Most of the groundwater wells are located in the immediate vicinity of the streams. The depths of the groundwater wells vary from 3 to 270 m and the elevation of the water table closely mimics the land surface topography.

Mean annual precipitation during 1966–1999 was 1020 mm in this area; this is slightly lower than the mean value of 1270 mm for the whole country. Of the total precipitation, 64% occurs in the wet season (June–September), which is a characteristic of the monsoon climate of eastern Asia (Lee & Lee 2000). The average annual air temperature for the past 10 years was 11.2 °C. A rockfill dam with a storage capacity of 48.7×10^6 m^3 will be built for flow control and public water supply on an area about 11 km downgradient of the mine waste dump, which is located within 6 km upgradient from the uppermost edges of the planned submerged area owing to dam construction. Concerns about the potential harmful effect of the abandoned mine on the quality of water stored behind the planned dam initiated a comprehensive environmental study including soils, sediments, surface waters and groundwaters.

Methods and materials

Groundwater well field

The mine portal is located in a small mountainous valley (see second inset in Fig. 1). The topographic levels range between 400 and 500 m above mean sea level. There is a waste dump (tailing and refuse pile) with a volume of 5000 m^3, which is 500 m downgradient from the mine portal where effluence of mine water still occurs at rates of 5–10 m^3 day^{-1}. Despite some environmental remediation activities in 1998–1999, some untreated mining wastes still were piled up in the vicinity of the mine portal, and some portions of the reclamation area were damaged.

To evaluate the hydrogeological conditions and groundwater chemistry especially in and around the waste dump, a well field comprising seven monitoring wells was constructed (see the second inset in Fig. 1). The wells were installed at depths of 25–85.5 m. Stratigraphic units underlying the site include Cretaceous sedimentary rock intruded by Cretaceous granite, and covered by colluvial soil and a local reclamation layer. The surface soil is observed at depths ranging from 0 to 2 m below the ground surface. The weathered rock ranging between 2.5 and 4 m below ground surface has

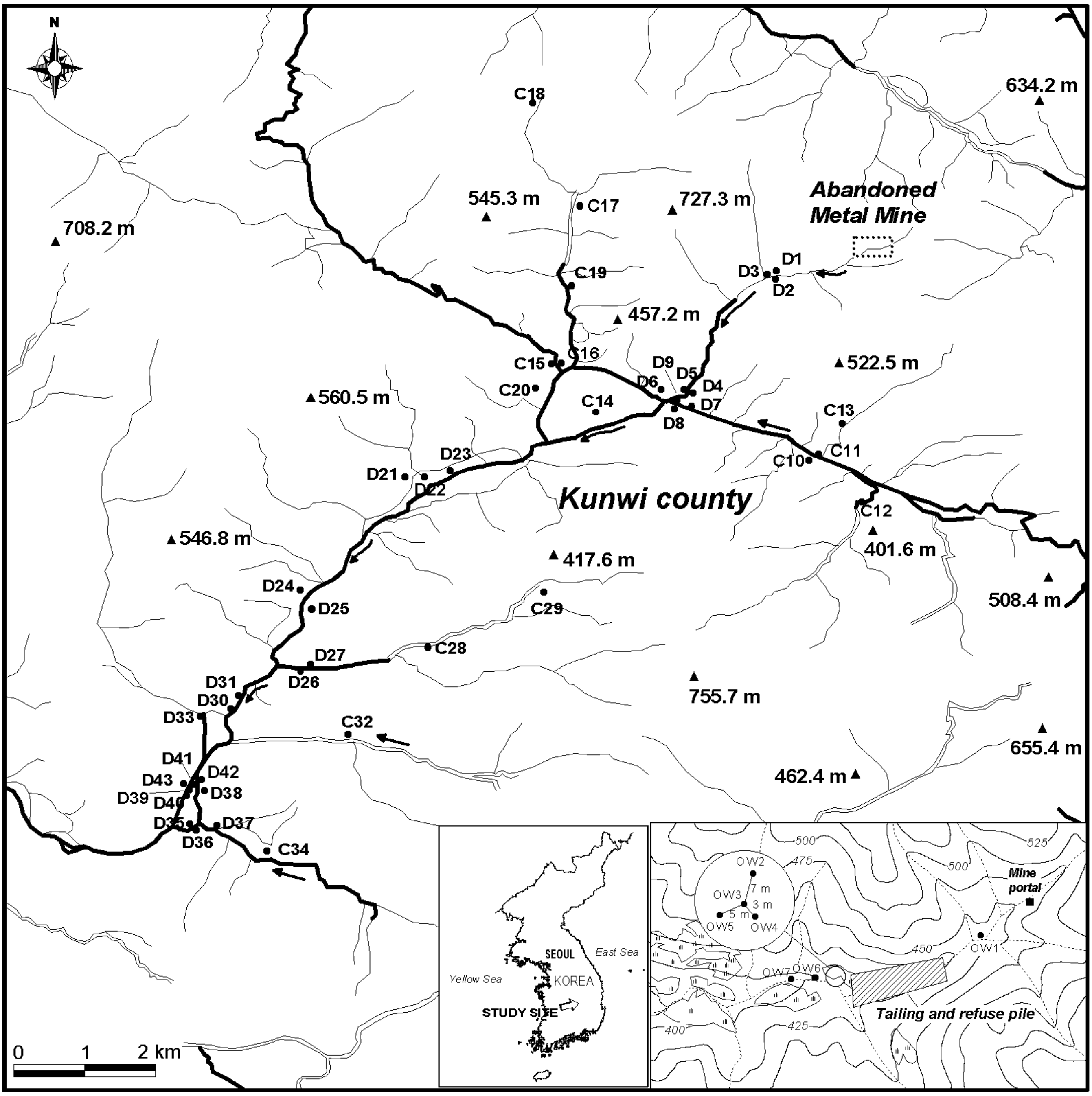

Fig. 1. Locations of the study site and the groundwater sampling locations. The abandoned metal mine location is also shown. Arrows indicate general water flow direction. The second inset illustrates layout of the newly installed groundwater monitoring wells, mine waste dump (tailing and refuse pile) and mine portal.

secondary permeability features and is hydraulically connected to the colluvial deposits and/or reclamation layer. The weathered zone is underlain by the soft rock. This unweathered zone extends from 4 to 19 m below the ground surface. Below the soft rock, hard rock exists. This relatively impervious layer serves as a lower confining bed for the upper aquifer.

The well field has one deep observation well of about 85.5 m depth (OW3) and six shallow observation wells of 25–26.5 m depth (OW1, OW2 and OW4–OW7). All the wells were cased to the bottom of the weathered zone, and left unlined below. They were all installed within a very small area. Only well OW1 was installed between the mine portal and the waste dump (see the second inset in Fig. 1). The water levels of the monitoring wells occur at an average depth of 5.27 m below the surface. In the well field, a total of 14 slug tests and two short-term pumping tests were conducted. Furthermore, a single well drift–pumpback tracer test was conducted using bromide and rhodamine WT. Two rounds of water-level measurement were also conducted in February and March 2003 to evaluate groundwater flow conditions.

Groundwater chemical analysis

The groundwater wells are suitable for obtaining water samples for chemical analyses and also have a water-level measurement opening according to the Groundwater Act of South Korea. To examine chemical compositions and toxic metal contamination of the groundwaters in the study area, water samplings at 43 private and public groundwater wells from a total of 70 wells along the NE–SW transect of the area and at seven newly installed groundwater wells near the mine waste dump were performed in January 2003 (see sampling locations in Fig. 1). At least three well volumes of water were purged before sampling, using a low-rate submersible pump attached to a polyethylene (PE) hose, which was connected to a closed flow-through cell.

Prior to water sampling for laboratory analysis, the temperature (*T*), pH, electrical conductivity (EC) and dissolved oxygen (DO) were measured with standard probes in the cell. Samples were collected only when the values stabilized. Water samples for the laboratory analysis were collected directly from the unbroken water stream. Samples for multi-element analysis were syringe-filtered at 0.45 μm and preserved using ultra-pure HNO_3 in 125 ml high-density polyethylene (HDPE) bottles. Samples for laboratory analysis for anions were collected in 60 ml HDPE bottles through a 0.45 μm syringe filter. All samples were stored at 4 °C until analysis. At least 10% of the samples were spiked and duplicated.

Anions (NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}, SO_4^{2-}, F^-, Cl^- and Br^-) were analysed by ion chromatography (IC, DX-120, DIONEX), except for bicarbonate (HCO_3^-), which was determined by titration. Cations (Al, K, Ca, Mn, Si, Mg, Na, Cr, Fe, Cu, Zn, As, Cd and Pb) were analysed by inductively coupled plasma-mass spectrometry (ICP-MS, Ultramass 700, Varian), atomic absorption (AA, 5100PC, Perkin Elmer) and ICP (ICP-1000 IIIS, Shimadzu) following EPA standard methods.

Factor and cluster analysis

Factor analysis attempts to simplify the complex and diverse relationships that exist among a set of observed variables by revealing common and unobservable factors that link the seemingly unrelated variables (Usunoff & Guzman-Guzman 1989; Evans *et al.* 1996). In hydrogeological studies, the results of groundwater chemical analysis and field measurement data are the observable variables, and the underlying physicochemical and/or biological processes in the groundwater system are the so-called unobservable common factors.

Cluster analysis groups the whole groundwater system into a finite number of clusters. Each cluster represents a specific and similar hydrogeochemical state of groundwater. Usually, cluster analysis is applied to the raw data (the observable variables; see Frapporti *et al.* 1993; Ochsenkühn *et al.* 1997). In this study, the factor scores were used instead of the raw data, to prevent the cluster analysis from involving unnecessary or trivial factors and mutually dependent variables (Suk & Lee 1999; J. Y. Lee *et al.* 2001). For the multivariate analyses, the SAS® package (SAS Institute, Inc. 1997) was used.

Results and discussion

Hydrogeological characteristics in the abandoned mine

The distribution of water levels in and around the waste dump measured in February and March 2003 is shown in Figure 2. Water levels at OW4 and OW5 (relatively more proximal to the creek) were higher than those at OW3 and OW2 (more distal to the creek) in February 2003 (Fig. 2a). Excepting OW1 and OW6, water levels at the wells were lower than the water level of the creek. In the bottom area of the barrier wall of the tailing and refuse pile where OW4 and OW5 are located, the creek recharges groundwater, whereas groundwater flows into the creek in the area where OW6 is located. In the gaining stream, water-level contours crossing the stream form a V shape but in the losing stream, they form an inverted V shape. The losing stream in the immediate vicinity of the barrier wall occurred during periods of peak flow of the creek as a result of snowmelt runoff. Natural creeks and surrounding groundwater aquifers are usually in dynamic contact with each other and a creek or stream that is normally a gaining stream will become periodically or spatially a losing stream during short flood events (Fetter 2001; Koch & Rachidi 2001). This can pose, especially in this case where the creek water is contaminated with toxic metals, the threat of groundwater pollution. The same pattern was shown in the water levels measured in March 2003 (see Fig. 2b), but the water levels were partly elevated compared with those in February.

Estimates of hydraulic conductivity from the slug tests ranged from 2.20×10^{-5} to 3.07×10^{-4} cm s^{-1} with a geometric mean of 7.56×10^{-5} cm s^{-1}. Upper values of the hydraulic conductivity estimates appeared somewhat larger for the moderately fractured rock. Furthermore, a larger variation of the hydraulic conductivity values over one order of magnitude indicated somewhat inherent heterogeneity of the subsurface. From the pumping tests, an average hydraulic conductivity of 3.66×10^{-5} cm s^{-1} and a storativity of 2.7×10^{-3} were obtained. In addition, based on the observed breakthrough curves of the tracer test, average linear groundwater velocity and effective porosity were estimated as 1.71×10^{-1} m day^{-1} and 0.037, respectively.

Groundwater geochemistry

For comparison purposes, the 50 sampling locations are classified into mine area samples (OW series wells,

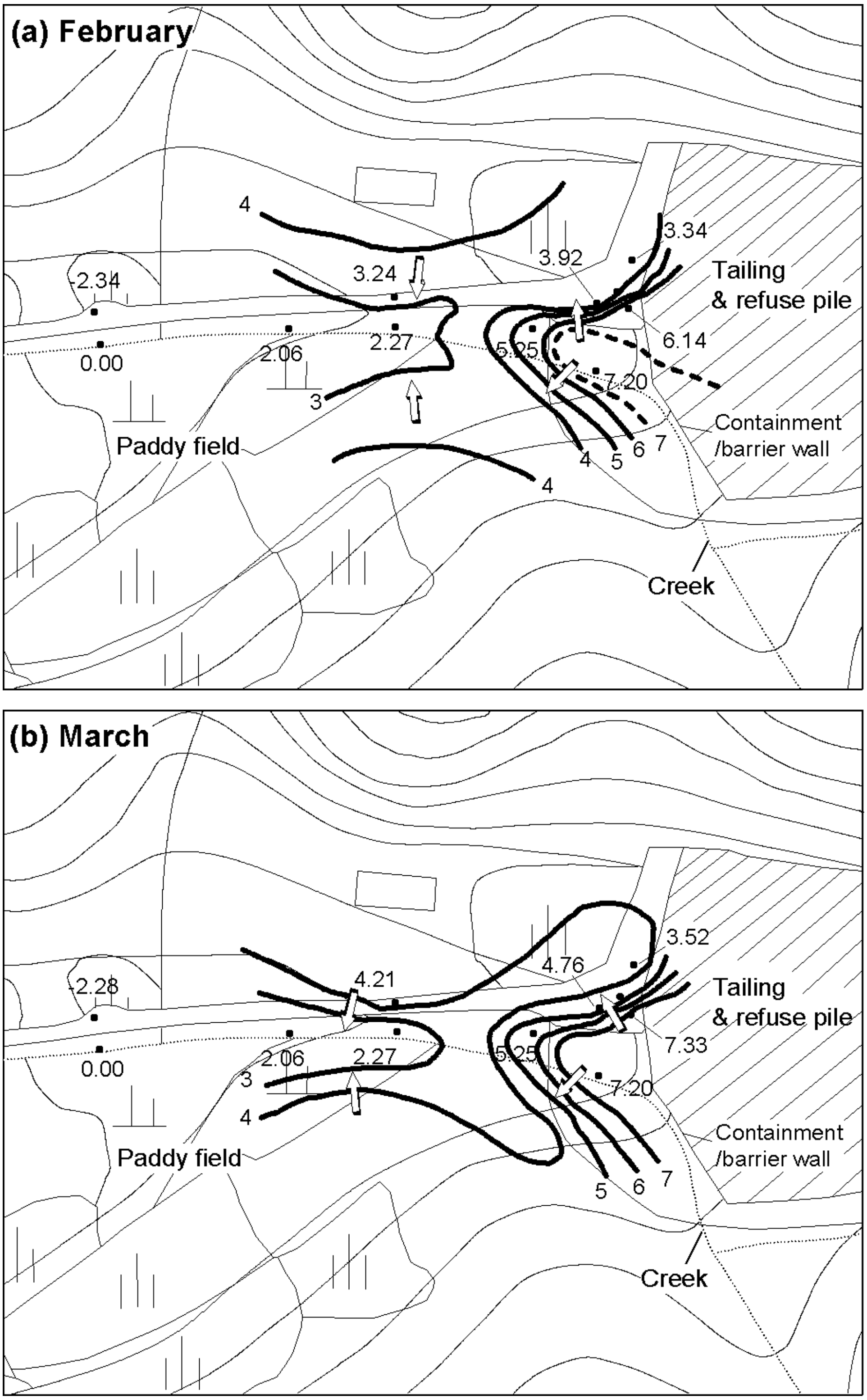

Fig. 2. Water-level distribution in and around the waste dumping site. The heads are represented by relative altitude. Arrows indicate groundwater flow direction. Creeks are represented by dotted lines.

n = 7), downstream area samples (D series wells, *n* = 28), and comparison or control area samples (*n* = 15) (see sampling locations in Fig. 1). The comparison or control wells, which reflect background, non-affected or non-contaminated water chemistry (but not completely), were selected based on consideration of topography, stream water flow direction and soil contamination data. Soils (mostly in paddy fields) immediately adjacent to the main stream in the downstream area were affected by toxic metal contamination including arsenic (As),

Table 1. *Summary of physical properties, chemical compositions, and toxic metals or metalloids of the groundwaters.*

Species	Minimum	Maximum	Mean	SD	CV	NC	DIS
pH	6.2	8.2	7.3	0.4	0.06	0 (0)	Normal
T (°C)	1.8	17.3	9.4	3.5	0.37	0 (0)	Normal
EC (μS cm^{-1})	77	871	316	176	0.56	0 (0)	Normal
DO	3.8	9.9	7.8	1.8	0.24	0 (0)	Normal
Ca	6.20	116.28	29.52	22.43	0.76	0 (0)	Normal
Mg	1.50	24.48	7.84	4.91	0.63	0 (0)	Normal
Na	4.70	33.20	13.86	7.39	0.53	0 (0)	Normal
K	0.45	10.46	1.58	1.61	1.02	0 (0)	Log normal
NH_4	ND	2.41	0.08	0.35	4.34	29 (58)	NA
Si	1.35	13.66	8.77	2.93	0.33	0 (0)	Normal
Br	ND	1.28	0.05	0.23	4.92	48 (96)	NA
Cl	3.45	45.10	12.42	9.26	0.75	0 (0)	Normal
F	ND	0.50	0.16	0.12	0.72	10 (20)	NA
NO_2	ND	0.35	0.01	0.05	6.56	49 (98)	NA
NO_3	ND	106.70	18.60	24.36	1.31	2 (4)	Log normal
PO_4	ND	NA	NA	NA	NA	50 (100)	NA
SO_4	5.60	392.86	49.74	89.11	1.79	0 (0)	Log normal
HCO_3	2.00	97.48	15.00	20.06	1.34	0 (0)	Log normal
COD_{Mn}	ND	4.40	1.03	0.89	0.87	8 (16)	NA
Al (μg l^{-1})	ND	4680	612	1815	1.51	33 (66)	200[1]
Cr (μg l^{-1})	ND	ND	NA	NA	NA	50 (100)	50[1]
Mn (μg l^{-1})	ND	8286	573	3009	1.81	29 (58)	300[1]
Fe (μg l^{-1})	ND	2280	272	759	1.15	16 (32)	300[1]
Cu (μg l^{-1})	ND	84	30	23	0.75	41 (82)	1000[1]
Zn (μg l^{-1})	4	11280	514	1014	0.89	0 (0)	1000[1]
As (μg l^{-1})	ND	47	15	14	1.74	37 (74)	50[1]
Cd (μg l^{-1})	ND	17	11	7	1.28	47 (94)	10[1]
Pb (μg l^{-1})	ND	90	49	3	1.32	48 (96)	50[1]

Units are mg l^{-1} unless otherwise noted. SD, standard deviation; CV, coefficient of variation; NC, number of censored values (proportion %); DIS, distribution of data values, P <0.05; ND, not detected, below detection limit 1 μg l^{-1} (censored value); NA, not available; COD, chemical oxygen demand.

[1] South Korean drinking water standards (μg l^{-1}).

cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) to varying degrees (Lee *et al.* 2003).

Field measured parameters are presented in Table 1. The temperature of the groundwaters ranged from 1.8 to 17.3 °C. The pH values for the waters were near neutral to slightly basic, with an apparent increase along the main stream flow direction. The lowest pH value of 6.2 was observed at OW5 near the waste dump. The relatively high values of pH may be due to the sparse abundance of pyrite; although sphalerite (ZnS), galena (PbS) and chalcopyrite ($CuFeS_2$) are more common in the mine area they release little acidity when weathered, and reaction with carbonate minerals (Hornberger *et al.* 1981; Williams *et al.* 1982; Perry & Brady 1995) and cyanides, by-products of mineral processing for Au and Ag (Jung 2001) also neutralizes pH. There is a statistically significant difference (P <0.05) in average pH values between the mine area and the other two areas, although all the pH values are within the South Korean drinking water standards (pH 5.8–8.5).

In comparison with groundwaters from the downstream and comparison areas, higher values of EC ranging from 149 to 871 μS cm^{-1} with a mean of 532 μS cm^{-1} were observed (P <0.05) in the mine area, which were closely related to high concentrations of dissolved solutes produced by weathering of tailing minerals. The EC values apparently decreased with distance from the mine, which indicated the removal of ions in the flow direction. The EC values were strongly positively correlated with concentrations of Ca^{2+}, Mg^{2+} and SO_4^{2-} (r^2 >0.80, P <0.05). Measured DO concentrations of >5 mg l^{-1} clearly indicated an oxygenated groundwater environment (Schulze-Makuch *et al.* 2003). Only at five groundwater wells (D4, D30, D38, D39 and C11) out of 50 sampling locations were DO concentrations below 5 mg l^{-1}, but the groundwaters were still aerobic (3.8–4.7 mg l^{-1}).

Relatively lower values for pH and higher levels of EC were found in the groundwaters passing through the mining waste dump. In the overall study area, it generally appeared that relatively high values of pH and DO concentrations were closely related to retarded migration of the toxic metals (see the toxic metals section below). The high pH of the groundwater (>7) may enhance toxic metal precipitation (Travainen *et al.* 1997; Salameh *et al.* 2002). As a whole, the field parameters of the mine area are very different from those of the other two areas.

The average concentrations and ranges of the major ions in groundwaters are also presented in Table 1. The most abundant cations and anions are Ca^{2+} and SO_4^{2-}, respectively, throughout the area. The combined Ca^{2+} and SO_4^{2-} concentrations make up the greatest portion of the total mass of ions, on average 47.6% of the total ionic species for the groundwaters. The high concentration of sulphate was derived from weathering and oxidation of sulphide minerals especially in the mine area. Relative ionic abundances in the groundwaters at the mine area show the trend $SO_4^{2-} > HCO_3^- > NO_3^- > Cl^- > Br^- > NO_2^- > F^-$ for the anions and $Ca^{2+} > Mg^{2+} > Na^+ > K^+ > NH_4^+$ for the cations. Sodium and chloride were relatively enriched in the downstream and comparison areas although calcium and sulphate were still most dominant.

NO_3^- and Cl^- were much more abundant in the groundwaters in the downstream and comparison area, which ranked second and third, whereas amounts of HCO_3^- ranked second in the groundwaters at the mine area. The relatively high concentrations of nitrate and chloride in groundwaters in the downstream area reflect, to some extent, inflow of surface water into the aquifer and/or anthropogenic effects derived from application of chemical fertilizers and livestock manure for cultivation mainly along the stream. Br^- and NH_4^+ are present generally in low concentrations or below the detection limit ($1\ \mu g\ l^{-1}$) in all the groundwater samples (see Table 1). PO_4^{3-} is below the detection limit. Substantial decreases in concentrations of calcium and sulphate along with total dissolved solids (TDS) or EC were observed in the downstream area.

One of the plausible explanations for apparent calcium and sulphate removal is dilution as a result of mixing with Ca^{2+}- and SO_4^{2-}-poor groundwaters (Rose *et al.* 1995; Schulze-Makuch *et al.* 2003), which was evidenced by a large increase in a conservative tracer ion (Cl^-) concentrations along the flow path. Removal of calcium and sulphate as a result of precipitation of gypsum under oxygenated conditions is highly unlikely given that the saturation indices did not indicate supersaturation. Reduction of sulphate to H_2S would not be expected either because the groundwaters in the downstream area remain aerobic (Hem 1992; Schulze-Makuch *et al.* 2003). In the relatively nutrient-poor environment, represented by low total organic carbon ($<1.0\ mg\ l^{-1}$) and phosphate ($1< \mu g\ l^{-1}$), little oxygen is used up by subsurface micro-organisms for their metabolic needs (Aykol *et al.* 2004), and anaerobic conditions do not develop.

The results of plotting 50 groundwater samples on a Piper diagram are shown in Figure 3. The groundwaters are mostly classified into four types including Ca + Mg–Cl + SO_4, Ca + Mg–Cl + HCO_3, Ca + Na–Cl + HCO_3, and Ca + Na–Cl + SO_4. The most dominant Ca–SO_4 type represents effects of dissolution of carbonate and sulphide minerals. Enrichment of bicarbonate also indicates that dissolution of carbonate minerals occurred locally in the basement metasedimentary rocks. Only two groundwater samples show somewhat different types, Ca + Na–HCO_3 + Cl + SO_4 type for well OW3 and Na + Ca–Cl + SO_4 for well D39. Well OW3 was most deeply installed and opened to a depth of 85.5 m compared with the other six wells (OW series, 25–26.5 m depth), so the groundwater at well OW3 may reflect some mixed chemistry of shallow and relatively deep waters. The reason for the somewhat different type for well D39 is not known. The groundwater geochemistry changes along the flow path from Ca^{2+} and SO_4^{2-} being dominant in the mine-affected area to less Ca^{2+} and SO_4^{2-} or Na^+ and Cl^- relatively more enriched in the downstream area. Increase in chloride concentrations reflects anthropogenic effects or inflow of surface water into the nearby aquifer.

Although the OW wells were located within a small area, the Piper diagram shows some variations in water geochemistry in the area. The groundwater geochemistries, inferred from the diagram, of the wells (OW2–OW5) closest to the mine waste dump are very different from those of OW1 (most upstream) and OW6 and OW7 (somewhat downstream). Multiple comparison using the Tukey method revealed that the means of major ions including Ca^{2+} and SO_4^{2-} were statistically different at $P < 0.05$ among the groundwaters from the three sample groups (OW2–OW5; OW1, OW6 and OW7; D and C series wells).

Factor analysis

An exploratory investigation of the groundwater chemistry data was performed prior to an initial factor analysis. The Shapiro–Wilk normality tests (Shapiro & Wilk 1965) and box plots were included in this investigation to identify abnormal values or outliers (see Table 1). The Shapiro–Wilk tests showed that some of the parameters of interest including pH, T, EC, DO, Ca, Mg, Na, K, Si, Cl, NO_3, SO_4 and HCO_3 showed a normal distribution at $P = 0.05$ without or with the log transformation that has been commonly applied to hydrochemistry data (e.g. Reimann & Filzmoser 2000; Carlon *et al.* 2001). Based on the exploratory data analysis, the data for each selected groundwater parameter were standardized and scaled to equalize the influence of parameters with small and large variations using the z transformation (Auf der Heyde 1990; Ravichandran *et al.* 1996). The calculated z scores were used as input for the factor analysis. Thirteen variables from a total of 19 observed parameters were adopted for initial factor analysis. The six parameters NH_4, Br, F, NO_2, PO_4 and chemical oxygen demand (COD) were excluded because of non-normal distribution of the data mainly derived from censored values.

Table 2 shows the correlation matrix of z scores for the 13 variables from the groundwater data.

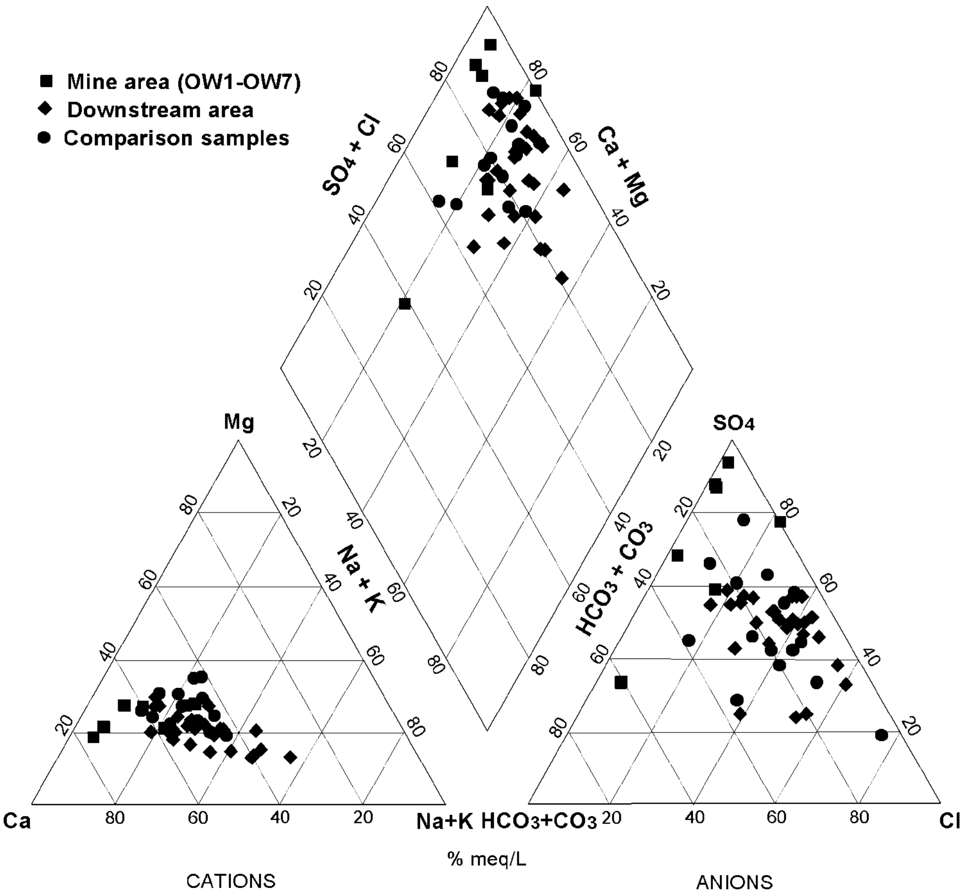

Fig. 3. Piper diagram showing compositions of major ions for the groundwaters in the mine, downstream and comparison areas. Symbol size does not indicate the magnitude of total dissolved solids (TDS).

Table 2. *Correlation matrix of 13 variables computed from physical and chemical analyses data.*

	pH	*T*	EC	DO	Ca	Mg	Na	K	Si	Cl	NO_3	SO_4	HCO_3
pH	–	−0.27	−0.29	−0.10	−0.35	−0.21	0.50	−0.46	0.01	−0.05	−0.37	−0.49	−0.04
T		–	0.05	−0.30	0.10	0.03	−0.21	0.09	0.05	0.08	0.40	0.10	0.09
EC			–	−0.27	**0.97**	**0.91**	0.24	0.18	0.58	0.19	−0.03	**0.85**	**0.63**
DO				–	−0.25	−0.19	−0.41	0.24	−0.21	−0.19	0.08	−0.33	−0.29
Ca					–	**0.86**	0.07	0.22	0.46	0.05	−0.01	**0.86**	**0.63**
Mg						–	0.16	0.11	**0.68**	0.28	−0.05	**0.72**	**0.60**
Na							–	−0.30	0.38	0.21	−0.39	0.06	0.19
K								–	−0.20	0.07	0.15	0.29	0.04
Si									–	0.30	0.01	0.35	0.50
Cl										–	0.38	0.00	−0.25
NO_3											–	−0.01	−0.23
SO_4												–	**0.64**
HCO_3													–

Values greater than 0.6 are in bold type.

Interestingly, the pH values do not show any significant correlation with the other parameters. In fact, a meaningful correlation can be expected between the pH and the parameters including EC, dissolved solids, sulphate and/or toxic metal concentrations (Cambier & Charlatchka 1999; Kelly *et al.* 2004). However, there is a discernible correlation only in groundwaters in the mine area. Significant correlations over 0.80 were found between EC and Ca, Mg and SO_4, and Ca and Mg and SO_4. From the observed hydrochemical characteristics along with major mineral constituents in rocks and ores, it was suggested that the groundwaters evolved largely through dissolution of sulphide and carbonate minerals with a lesser degree of silicate minerals (C. H. Lee *et al.* 2001).

Based on the computed correlations between the 13 variables, and in the context of geochemical importance,

Table 3. *Eigenvalues of factors extracted through principal component analysis, differences between factors, and proportions of variance explained by the factors.*

Factors	Eigenvalue	Difference	Proportion	Cumulative
1	4.7838	2.2812	0.3680	0.3680
2	2.5025	0.8621	0.1925	0.5605
3	1.6405	0.4024	0.1262	0.6867
4	1.2381	0.4004	0.0952	0.7819
5	0.8376	0.2592	0.0644	0.8463
6	0.5784	0.1750	0.0445	0.8908
7	0.4034	0.0226	0.0310	0.9219
8	0.3808	0.0908	0.0293	0.9512
9	0.2899	0.1019	0.0223	0.9735
10	0.1881	0.1008	0.0145	0.9879
11	0.0872	0.0237	0.0067	0.9947
12	0.0635	0.0576	0.0049	0.9995
13	0.0059	–	0.0005	1.0000

all 13 variables (pH, *T*, EC, DO, Ca, Mg, Na, K, Si, Cl, NO_3, SO_4 and HCO_3) were selected for the final factor analysis. The results indicated that only four factors were needed to explain about 80% of the total variance (Table 3). Furthermore, the final communality was appropriately assigned to each variable (data not shown). Table 3 shows the eigenvalues of the extracted factors, the eigenvalue difference among the factors, and the proportion of total sample variance explained by the factors. The first four factors were selected to represent the hydrochemical processes of the groundwater, without losing significant information. The selection of the four most important factors is based on the eigenvalue criterion (>1) and the variance explained by the extracted factors. As previously noted, the first four factors explain about 80% of the total sample variances. For a simpler and easier interpretation, factor rotation was performed using varimax rotation after factor extraction.

The rotated factor pattern of the four factors is shown in Figure 4. Factor 1 explains the largest proportion (37%) of the total variance. There are high positive loadings for EC, Ca, Mg and SO_4, and moderately positive loading for HCO_3. This factor is associated with groundwaters with high concentrations of Ca, Mg, SO_4 and HCO_3. In other words, Factor 1 is globally indicative of the hydrochemistry of groundwaters affected by preferential dissolution of sulphide and carbonate minerals, which are included in the compositions of the ores and the bedrock, with a lesser degree of silicate minerals, and largely occur in the mine area (Lee *et al.* 1999; C. H. Lee *et al.* 2001). Water with high concentrations of SO_4 may originate from the mine waste dump, as shown by the highest scores of Factor 1 in the groundwaters in the mine area (Fig. 5). The ubiquitous distribution of low or negative scores of Factor 1 in the downstream area also supported this explanation. The highest loadings of Factor 1 are located at wells OW2, OW4 and OW5. Interestingly, well OW1 well, located in the immediate downgradient from the mine portal, showed a negative score for Factor 1, which indicated that the groundwater at that well was not affected by acid mine drainage or dissolution of sulphide minerals.

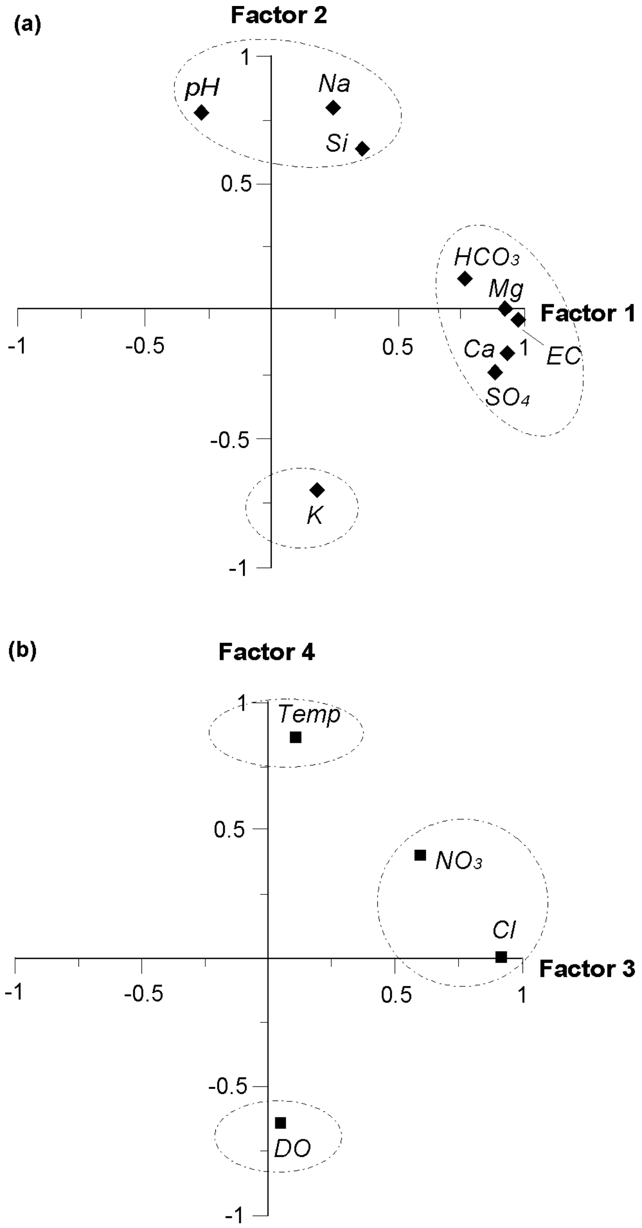

Fig. 4. Rotated factor pattern of five extracted factors after varimax rotation.

Factor 2 accounts for the major part of the variances of Si, Na and pH, whereas it is negatively correlated with K. Values of pH would increase in an area not affected by the mine waste. It seems probable that most of the dissolved Si observed in the groundwater originally resulted from the dissolution of silicate minerals by processes of weathering (Hem 1992). Multiple geochemical processes involving the increase of pH, Na and Si can largely be characterized by Factor 2. The main sources of Na may be igneous rock including

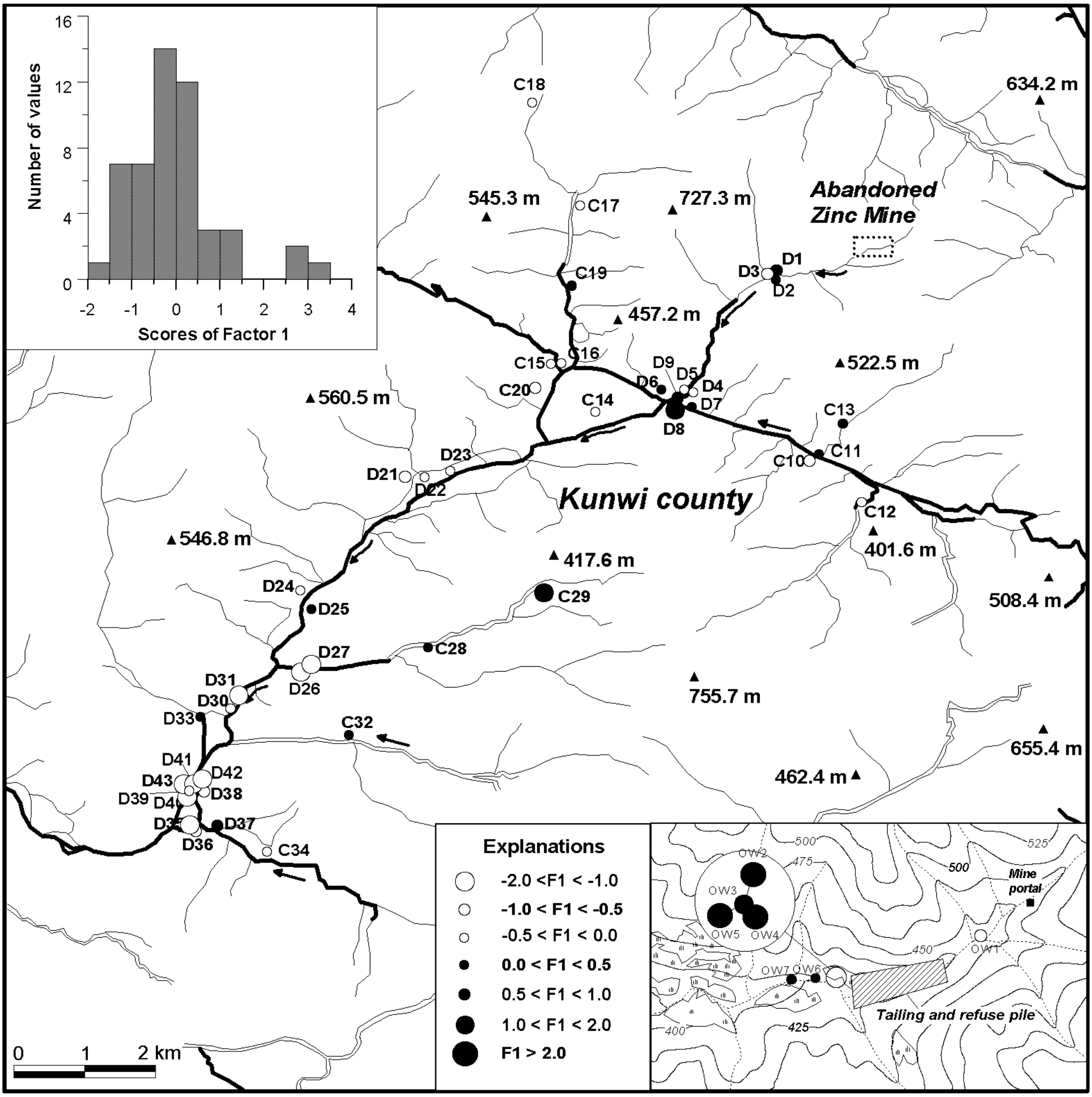

Fig. 5. Areal distribution of factor scores for Factor 1.

feldspar minerals. Sodium tends to remain in solution rather persistently once it has been liberated from silicate minerals whereas potassium exhibits a strong tendency to be reintroduced into solid weathering products (certain clay minerals); consequently, in most natural groundwaters, the concentration of potassium is somewhat or much lower than that of sodium (Hem 1992; see Table 1). The negative loading of K for Factor 2, to some extent, may be explained by the removal of K as a result of the reintroduction of plants and their uptake of K as an essential element.

Factor 3 has high positive loading for Cl and a moderately positive one for NO_3 (see Fig. 4b). These two parameters represent the highest or high concentrations in the upper part of the downstream area, where heavy agricultural activity has occurred. Random distribution except in this area and lower or negative factor scores in the mine waste area imply that these parameters are different from most constituents of Factor 1 in their origins, such as domestic sewage, agricultural chemicals, fertilizer and/or livestock manure (C. H. Lee *et al.* 2001; Fig. 6). Factor 3 is mostly associated with the increase in chloride and nitrate. The highest loadings of Factor 3 are located at D1, D8 and C19. Factor 4 is associated with groundwaters with low DO and high T values. High water temperatures are largely associated

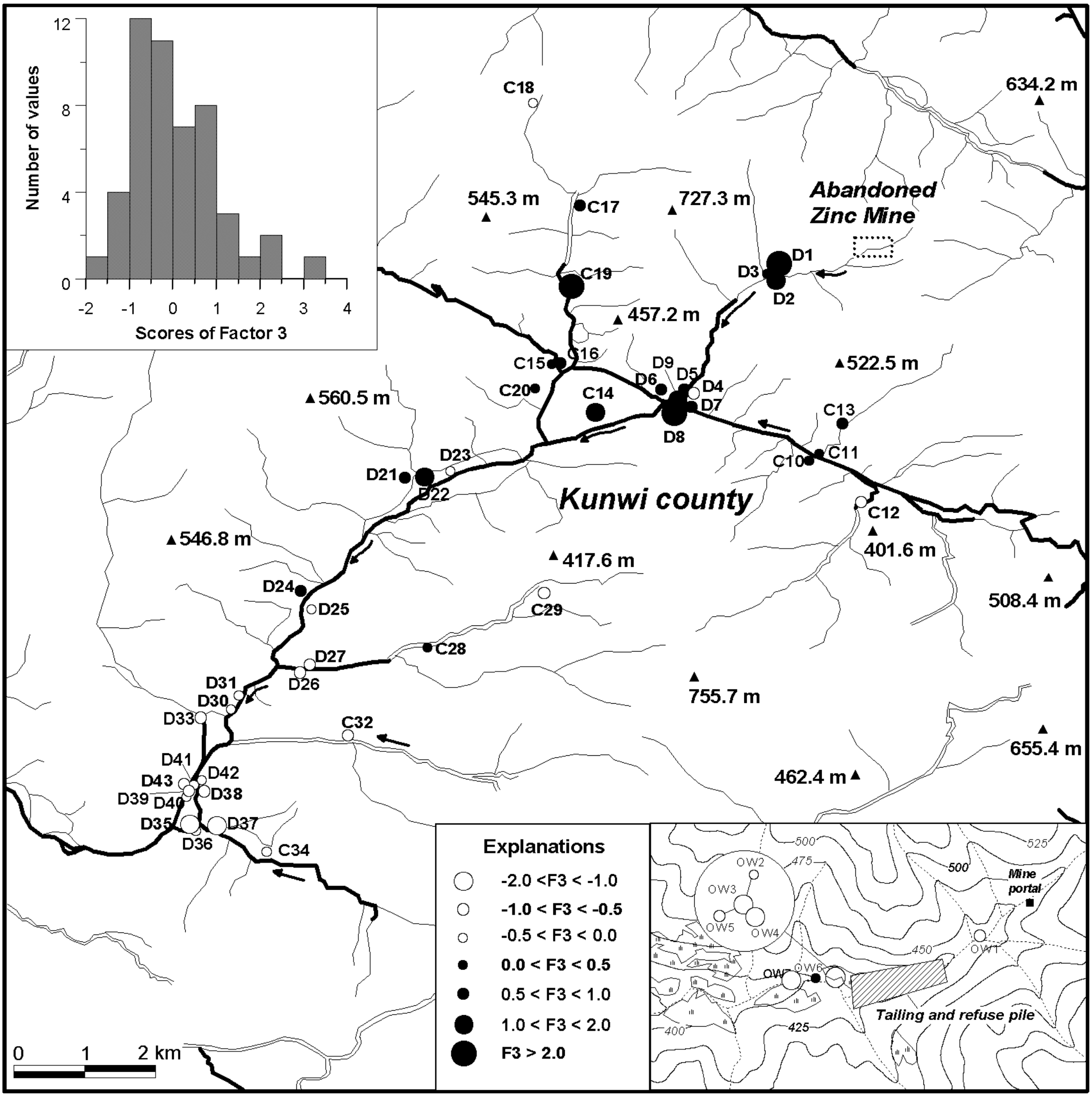

Fig. 6. Geographical distribution of factor scores for Factor 3.

with a shallow water table, which is related to the water recharged from rain. Generally, oxygen solubility in water is negatively related to water temperature. Decline in concentration of dissolved oxygen may be related to biodegradation. However, the low organic carbon contents and high positive redox potentials do not guarantee the occurrence of these processes. The large increase in DO indicates the infiltration or recharge of water with high levels of DO. Factor 4 has its largest positive loading for well OW3.

On the basis of the water chemistry and the factor analyses, the dominant mechanisms or continuing processes affecting the distribution of the geochemical parameters in the study area are various geochemical reactions including dissolution of sulphide and carbonate minerals, and calcium and sulphate removal by dilution as a result of mixing with Ca^{2+}– and SO_4^{2-}-poor groundwaters.

Cluster analysis

Cluster analysis was performed to split the water sampling points into a finite number of groups (zones) with similar hydrochemical composition. The resulting dendrogram for the groundwater samples is presented in

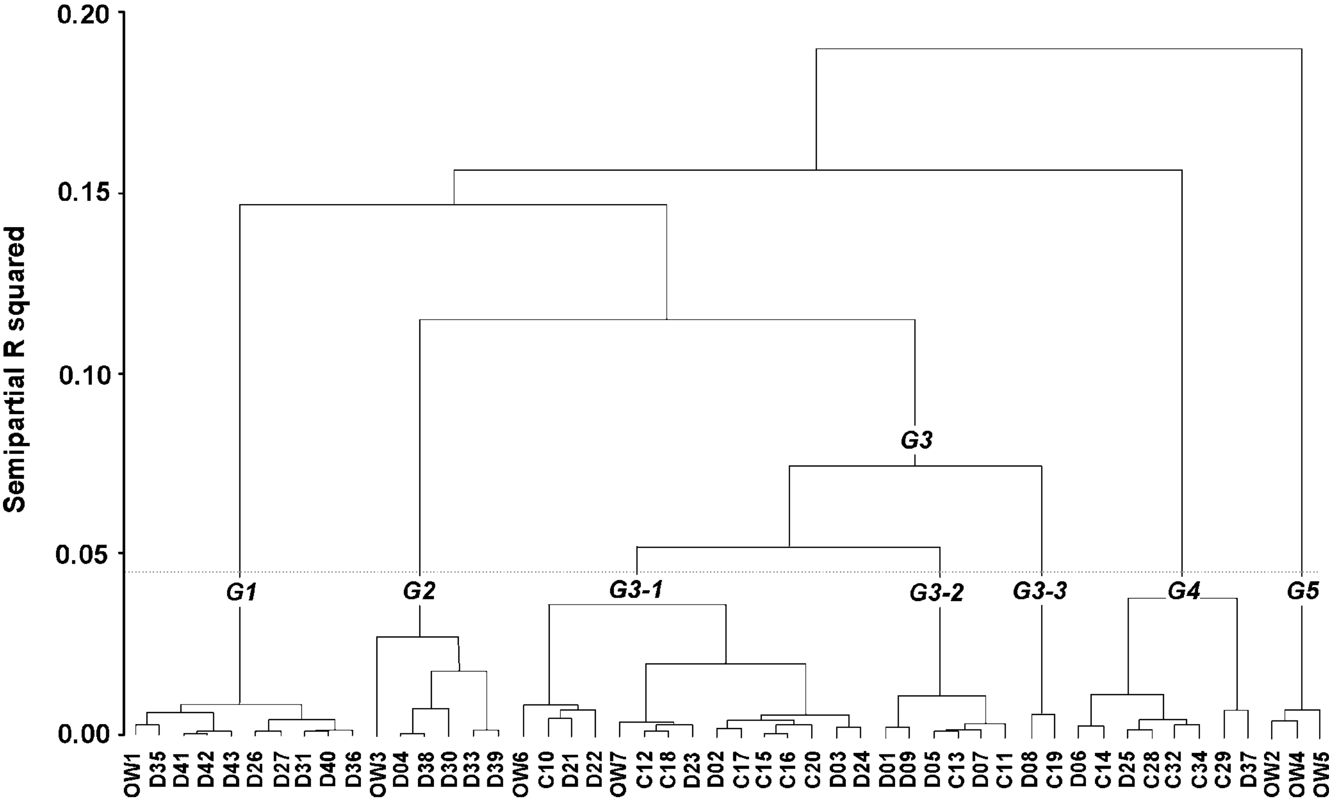

Fig. 7. Dendrogram formed using factor scores. Five main groups with similar chemical compositions are identified.

Figure 7. Five main groups were identified based on the overall structure of the dendrogram. Group 3 is further classified into three subgroups. The discriminant analysis guaranteed the appropriateness of the clustering. No misclassified observations were detected at a significance level of 0.05. Well OW2 is most upstream of the mine waste dump location and is slightly, or little, affected by the dissolution of sulphide minerals or mine waters. Therefore, it showed totally different groundwater chemistry. Consequently, that well was not classified into the same group as the mine area wells. Wells OW2, OW4 and OW5, which are close to each other, showed very similar groundwater chemistries. Interestingly, well OW3 is also not grouped into the cluster. As mentioned above, well OW3 is the deepest observation well (85.5 m) in the mine area, and this resulted in very different water chemistry. The other wells have an depth of 25 m.

The geographical distribution of the classified groups is presented in Figure 8. As shown in the figure, most interestingly, the groundwater wells, statistically grouped based on the similarity of chemical composition, did not show discernible geographical proximity. Only group 5 shows a strong correlation between water chemistry and geographical location. However, although there is an explicitly heterogeneous distribution of the grouped wells throughout the study area, some general geographical divisions are possible. Based on the geographical centre of the grouped wells, groups 5, 3-2, 3-3, 3-1, 4 and 2 = 1 exhibit increasing levels with radial distance from the mine portal. Furthermore, if G3 is considered as one group instead of three subgroups (G3-1, G3-2, G3-3) it appeared more distinct.

The hydrogeochemical parameters such as pH and EC characterizing each of these groups are summarized in Table 4. From the table, it can be seen that groups 5 and 1 show the most distinctive groundwater chemistry; group 5 represents the effects of the mining waste dump whereas group 1 shows mostly not affected or natural background water chemistry. Nevertheless, of the strict statistical classification of groups 2, 3 and 4, they do not significantly differ from each other with respect to major chemical compositions. Based only on the cluster analysis, it may be inferred that the effects of the mining waste on the groundwaters are restricted to only the immediate vicinity of the dump site but some chemical or physical evolution such as mixing has occurred during groundwater flow from upland to lowland areas.

Toxic metals in groundwater

The concentrations of toxic metals or metalloids in groundwaters at the study area are summarized in Table 1. Levels of some of them were relatively low whereas those of others were above the South Korean drinking water standards. The concentrations of these toxic metals are highly varable throughout the study area. High concentrations of the toxic metals including Al, Mn, Fe and Zn were observed in the groundwaters,

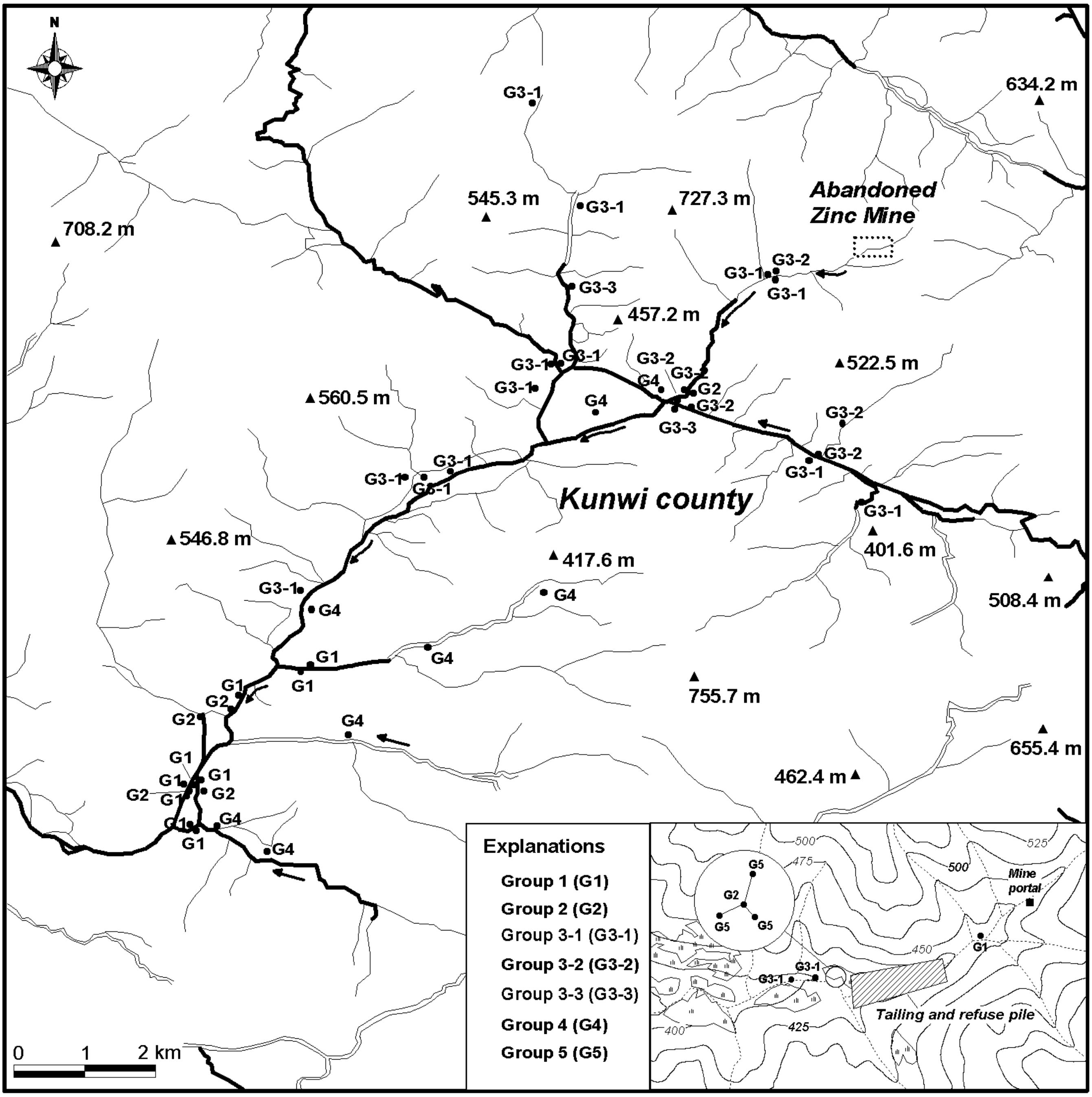

Fig. 8. Geographical distribution of the grouped groundwater wells from the cluster analysis.

especially in the mine area. The Al concentrations in the groundwaters at the mine area were from 50 to 4680 μg l^{-1} with a mean of 1204 μg l^{-1}. Aluminium concentrations above the South Korean guideline for drinking water (200 μg l^{-1}) were also observed at well D22, which is about 6 km away from the mine waste dump. The occurrence of the toxic metals at relatively remote locations may be attributed to runoff of rainfall, rapid transport by surface water and percolation to the aquifer, or ubiquitous geology (Salameh *et al.* 2002; Kelly *et al.* 2004). The maximum concentration (4680 μg l^{-1}) of Al was found at well OW6 in the mine area. The range and average concentrations of Al in the downstream area were from below detection limit to 1240 μg l^{-1} and 217 μg l^{-1}, respectively. In the comparison area, Al at 30 μg l^{-1} was found at only a single location (well C18). Interestingly, concentrations of Al were highly correlated with those of Fe ($r^2 = 0.91$ at $P < 0.01$).

In the mine area, the average concentrations of the metals were 1662, 661, 1130, 17 and 11 μg l^{-1} for Mn, Fe, Zn, As and Cd, respectively. Lead at 8 μg l^{-1} was observed only at well OW4. Concentrations of four elements (Al, Mn, Fe and Zn) of the nine metal analytes at the mine area were above the South Korean drinking water standards (see Table 1). Relative metal abundance

Table 4. *Summary of some major variables for the classified groups.*

Group	pH	EC	Ca	Mg	Cl	SO_4	HCO_3
G1 (10)[2]	7.2[3]	123	10.25	2.71	6.79	14.59	5.96
G2 (6)	7.7	310	25.90	6.44	7.04	47.90	26.06
G3 (23)[4]	7.3	318	28.42	8.21	17.72	30.43	12.69
G3-1 (15)	7.3	267	22.79	6.71	12.90	26.02	14.95
G3-2 (6)	7.3	395	39.65	10.28	21.82	40.60	8.93
G3-3 (2)	7.2	471	36.90	13.30	41.60	32.70	7.00
G4 (8)	7.9	357	31.32	9.68	11.21	25.08	12.31
G5 (3)	6.4	848	104.59	19.91	4.51	384.52	47.95

[1] Units are mg l^{-1} unless otherwise noted. EC, electrical conductivity (μS cm^{-1}).

[2] Number of member wells.

[3] Arithmetic mean.

[4] Sum of G3 subgroups = (G3-1) + (G3-2) + (G3-3).

in the groundwaters at the mine area shows the trend Mn > Al > Zn > Fe > As > Cd > Pb. The concentrations of Cu and Cr were below detection limits (<1 μg l^{-1}). In the downstream area, the average concentrations of the toxic metals were Al 217 μg l^{-1}, Mn 29 μg l^{-1}, Fe 192 μg l^{-1}, Cu 32 μg l^{-1}, Zn 490 μg l^{-1} and As 17 μg l^{-1}, and so the relative abundance sequence is Zn > Al > Fe > Cu > Mn > As. Lead at 90 μg l^{-1} was found at a single well (well D35). Cd and Cr were not observed in the groundwaters. In this area, the most abundant metal was Zn instead of Mn for the mine area.

Zinc concentrations in the comparison area ranged from not detected to 2533 μg l^{-1} with a mean concentration of 271 μg l^{-1}. The maximum concentration was observed at well C13 (see well location in Fig. 1). It was interesting that this high concentration was found at this location, which was considered as or expected to be the control area or uncontaminated. To some extent, wind action, the same background geology and mineralogy may explain this. In comparison with groundwaters in the mine and downstream areas, relatively low or very low concentrations of Al, Cr, Mn, Fe, Cu, As, Cd and Pb were found in the groundwaters at the comparison area (Al $\leq$30 μg l^{-1}, Cr <1 μg l^{-1}, Mn $\leq$48 μg l^{-1}, Fe $\leq$229 μg l^{-1}, Cu $\leq$30 μg l^{-1}, As $\leq$14 μg l^{-1}, Cd <1 μg l^{-1} and Pb <1 μg l^{-1}). Concentrations of all the analysed toxic metals except Zn were below the South Korean drinking water standards in this area.

Results of ANOVA (analysis of variance) indicate that there is a statistical difference among the average concentrations of major metals including Al, Mn, Fe and Zn in the mine, downstream and comparison areas (P <0.05). This means that the groundwaters in the downstream area were affected to a certain extent by the abandoned mine, although the groundwaters in the comparison area also contained some levels of the toxic metals, especially Zn. The relatively high background levels (not completely uncontaminated) were mainly derived from the same geology as in the mine area.

In general, most of the toxic metals decreased gradually or dramatically with distance from the mine, although some metals were also found in high concentrations in the downstream and comparison areas. Compared with the soil contamination levels (Lee *et al.* 2003), levels of groundwater contamination by toxic metals were relatively low, contrary to expectation. The low concentrations may be due to the high pH of the groundwaters (>7), the highly oxygenated conditions, which enhance toxic metal precipitation (Travainen *et al.* 1997; Salameh *et al.* 2002; Kelly *et al.* 2004), and mixing with groundwaters containing low metal concentrations, although in general the highest concentrations are in the mine area.

Summary and conclusions

This study evaluated the hydrochemistry and potential groundwater contamination by toxic metals derived from an abandoned metal mine using a chemical analysis of the groundwaters and a multivariate statistical analysis. For these purposes, a well field consisting of seven monitoring wells was established in a small mountainous valley in which a mine waste dump was located. A total of 50 groundwater samples were collected from the 43 domestic and public water wells and the seven monitoring wells in mine, downstream and comparison areas. The waters were analysed for major cations, anions and relevant toxic metals.

The pH values for the waters were near neutral to slightly basic, with an apparent increase along the main stream flow direction. Higher values of electrical conductivity ranging from 149 to 871 μS cm^{-1} with a mean of 532 μS cm^{-1} were observed in the mine area. Measured dissolved oxygen concentrations of >5 mg l^{-1} clearly indicated an oxygenated groundwater environment. The high concentration of sulphate was derived from weathering and oxidation of sulphide minerals. Relative ionic abundance in the groundwaters in the mine area showed the trend SO_4 > HCO_3 > NO_3 > Cl > Br > NO_2 > F for the anions and Ca > Mg > Na > K > NH_4

for the cations. The Ca–SO_4 type water was most predominant.

Results of the factor and cluster analyses indicated that the dominant mechanism or continuing processes affecting the distribution of the geochemical parameters in the study area are various geochemical reactions including dissolution of sulphide and carbonate minerals, and calcium and sulphate removal by dilution because of mixing with Ca- and SO_4-poor groundwaters. It was also inferred that the effects of the mining waste on the groundwaters were strictly restricted in the immediate vicinity of the waste dump but some chemical or physical evolution such as mixing has been occurred during groundwater flow from upland to lowland areas.

In the mine area, severe groundwater contamination by toxic metals including Zn, Al, Fe and Mn was observed. In general, most of the toxic metals decreased gradually or dramatically with distance from the mine, although some metals were also found in high concentrations in the downstream and comparison areas. Compared with the soil contamination levels, levels of groundwater contamination by toxic metals were relatively low. In this area, pyrites was sparse. Furthermore, the low concentrations may be due to the high pH of the groundwaters and highly oxygenated conditions, which reduced metal mobility, although in general the highest concentrations were in the mine area.

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